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# PERMEATION STUDIES OF CW AGENTS WITH FABRIC TREATED WITH 8-HYDROXYQUINOLINE

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Reactive fabrics were studied for the Integrated Protective Fabric System project. The goal of the project was to develop a protective garment that has a lower thermal burden on the wearer by allowing heat and moisture transport. The garment prevents exposure to outside chemical weapons agents (CWAs) by reacting or reducing permeation of the CWA. By adding a reagent or reactive catalyst to the fabric, permeation can be decreased. 8-Hydroxyquinoline and benzisothiazolinone were studied as reagents to decrease permeation. Headspace gas chromatography was used to measure permeation of fabrics treated with the reagents.

**15. SUBJECT TERMS**

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|---|---|---|
| Integrated Protective Fabric System (IPFS) | Reactive fabric | |
| Chemical weapons agents (CWAs) | 8-Hydroxyquinoline (8-HQ) | Benzisothiazolinone (BIT) |
| Headspace gas chromatography | Vial-in-vial | |

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PREFACE

The work described in this report was authorized under Contract No. W911SR-11-C-0047. This work was started in August 2011 and completed in November 2014.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of endorsement.

This report has been approved for public release.

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PERMEATION STUDIES OF CW AGENTS WITH FABRIC TREATED WITH 8-HYDROXYQUINOLINE


ABSTRACT

Reactive fabrics were studied for the Integrated Protective Fabric System (IPFS) project. The goal of the project is to develop a protective garment that has a lower thermal burden on the wearer by allowing heat and moisture transport. The garment prevents exposure to outside chemical weapons agents (CWA) by reacting or reducing permeation of the CWA. By adding a reagent or reactive catalyst to the fabric, permeation can be decreased. 8-Hydroxyquinoline (8-HQ) and benzisothiazolinone (BIT) were studied as reagents to decrease permeation. Headspace Gas Chromatography was used to measure permeation of fabrics treated with the reagents.


## 1.0 INTRODUCTION

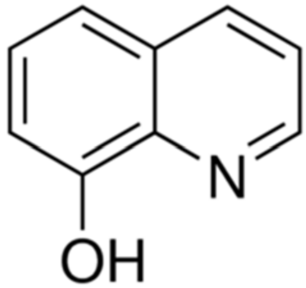
Reactive fabrics were studied for the Integrated Protective Fabric System (IPFS) project, with the goal of developing a protective garment that has a lower thermal burden on the wearer by allowing heat and moisture transport, by incorporating semi-permeable materials that allow transport of water vapor or air through the material in order to cool the wearer.[1] The garment prevents exposure to outside chemical weapons agents (CWA) or biological agents (BA) by a combination of absorption and reaction. In this report, only CWA reaction results are included.

By adding a reagent or reactive catalyst to the fabric, permeation of the CWA can be reduced. 8-Hydroxyquinoline (8-HQ) and benzisothiazolinone (BIT) were studied as reagents to decrease permeation of CWA. Headspace Gas Chromatography was used to measure permeation of CWA through fabrics treated with the reagents.

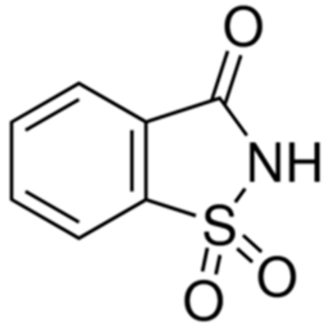
The CWA that were studied were bis(2-chloroethyl) sulfide (mustard or HD) and pinacolyl methylphosphonofluoridate (soman or GD). The fabrics to be tested are supplied by Natick Soldier Research Engineering and Development Center (SRDEC) as part of the IPFS project.

The development of 8-hydroxyquinoline (8-HQ) and benzisothiazolinone (BIT) as additives to outer shell fabric and to carbon cloth was done by Dr. Jeffery Owens (Tyndall Air Force Base, FL). These compounds have been approved for contact with human skin by the FDA, so they don’t present any hazard to wearers of a garment. They are known to be biocidal, which is sufficient reason to add them to the shell fabric to improve resistance to biological agents.

It was suggested that the compounds could have chemical reactivity against CWA as well, so a significant amount of testing was done to determine conditions under which they were reactive.



8-Hydroxyquinoline



Benzisothiazolinone (BIT)

## 2.0 EXPERIMENTAL METHODS

Several different experimental methods were used. The Headspace GC method is described briefly, and the specific procedures are given in other reports.

### 2.1 Headspace Vial-in-Vial GC Method

This test method is described in detail in a separate report.[2] In summary, this analytical chemistry method was developed for the IPFS project for measuring the reactivity and permeability of fabrics, films, and other solid materials. Headspace GC or GC/MS instrumentation is used. The method uses a small vial inside a larger headspace vial (known as the vial-in-vial method). The volatile agent is placed in a small inner vial, and the inner vial is capped with a layer of fabric or film to be tested. The agent permeates from the inner vial into an outer headspace vial by diffusion or permeation, without a pressure differential or flow of gas. The instrument equilibrates the vial at 40°C for 5 min. to increase the vapor pressure, and then it samples the vapor in the outer vial using a syringe and injects it into the GC for analysis. The presence of agent in the outer vial indicates that it has permeated through the film. Multiple sampling can be used to determine time dependence. Solids can also be tested for reactivity in the headspace vial without the inner vial, see Section 2.3.

Spiking was typically done using dilute solutions of agent (1-5 mg/ml), although neat agent could also be used. Solvent for HD was hexane, which was allowed to evaporate quickly to give a known small amount of neat agent in the inner vial.

After the headspace measurements were complete, the circle of fabric from the inner vial could be removed from the cap and placed in an autosampler vial; 500 µl of acetonitrile was added to immerse the fabric and extract any remaining analyte. The vial was vortexed for 30 sec. Immediately after, 1-2 µl of the liquid extract was injected on an Agilent GC/MS. The GC oven ramp is 50°C (1 min) ramped at 15°C/min. to 250°C.

## 2.2 Headspace GC Single Vial Method with Extraction

A variation on the headspace method, described in another report,[2] is to use only a single headspace vial. The material in the vial is spiked with CWA, and the headspace vapor of the CWA decreases as it reacts with the material. In summary, the following procedure is used:

1. A swatch of fabric to be studied was humidified to the desired conditions in a bottle with a water solution or DI water. Samples were cut to a size of 1 cm × 1 cm or weighed into the bottom of a headspace vial (10 or 20 mL total volume vial).
2. The fabrics were spiked with 1 µl of neat agent using a 5 µl syringe and a timer was started.
3. Samples of vapor (0.5 mL volume) from the headspace vials were automatically removed by an autosampler with a gas-tight syringe and injected into a Varian GC with a pulsed FPD detector. The GC method typically used a large split ratio during injection, since the amount of CWA vapor that was present could saturate the detector. The split flow is directed to a fume hood or a filter cartridge.
4. Calibration was done using small amounts of CWA in empty headspace vials or with solutions of agent in decane, which provides a constant partial pressure of CWA above the solution.
5. After reaction was complete or at a specified time, the fabric was extracted with a solvent, and the extract was analyzed using a liquid injection GC method.

## 3.0 8-HQ/BIT TREATED MATERIALS

Initial studies of NyCo fabric treated with 8-HQ showed a large decrease in permeation and so were very encouraging (Section 3.1). Positive results have also been obtained by testing at Tyndall AFB and Natick. However, subsequent testing on a number of samples shown some issues that affect the performance. One problem that was identified was that if fabric is heat treated, the 8-HQ/BIT may evaporate from the fabric. There also may be a large effect from the humidity of the fabric that could account for variation.

An additional problem was that the only analytical technique that measured fabric effectiveness was the Headspace vial-in-vial method, using vapor exposure of treated fabric to CWA or simulants. Efforts to identify reactions or products by NMR with liquid agent spiking on fabric or by reaction in solution were tried, but no reaction products were observed. 8-HQ is known to readily complex with metal ions, and this complexation could affect the reactivity.

As a result, the 8-HQ/BIT treated materials were found to be very effective in some cases, but the reaction data that shows the mechanism of its activity is limited.[3]

Most of the studies of 8-HQ/BIT treatments have been done on outer shell fabrics, such as cotton or NyCo (nylon/cotton blend). A study was also done of treated expanded PTFE (ePTFE), see Section 3.8.

## 3.1 First Results with 8-HQ

A study of the first batch of 8-hydroxyquinoline (8-HQ) treated cotton fabric, designated Batch #1, showed that the fabric was effective for reducing permeation of GD, DFP, and HD using Headspace GC/MS with the vial-in-vial method. Batch #1 was prepared at Tyndall AFB in July 2011,

and it was received from Heidi Schreuder-Gibson at Natick SRDEC in January 2012 and tested on Feb. 14-28. In the study, two replicates of untreated fabric and three replicates of treated fabric were analyzed in the order shown in Table 1. A quantity of 50 µg of GD was deposited in each of the inner vials, which was capped with a snap cap with a 0.25 in. diameter circle of the fabric sample. Fabric exposure to the agent is 50 µg/0.283 $cm^2$ = 0.2 mg/$cm^2$ = 2 g/$m^2$. The outer vials were sampled repeatedly with a headspace syringe for up to 5 days.

For the first 4 days, a low-sensitivity GC/MS method was used, and no signal was observed for the 8-HQ treated fabric samples. On day 5, the sensitivity was increased by using a SIM MS method and a larger volume sample. The numbers in Table 1 represent uncorrected GC/MS peak area TIC signal, in thousands of counts. A peak for GD was observed for the 8-HQ fabrics, but the signal may not be significantly higher than the background signal, so the GD signal for 8-HQ fabrics was 1.12% or less compared to the untreated fabrics. Results are plotted in a bar graph in Figure 1. The low signal for the treated fabrics indicates a significantly greater amount of reaction or absorption between the agent and the treated fabric compared to the untreated fabric in identical conditions.

For DFP and HD, the results were still promising, but not quite as good, shown in Table 2 and Table 3. For DFP, the signal for the 8-HQ fabrics was several times higher than the background signal. The signal for 8-HQ treated fabric decreased over time, from 11.3% at 8 hrs to 1.4% in 2 days.

For HD, the signal for the 8-HQ fabric samples was several times higher than the background signal, and the decrease relative to the untreated samples was 10.7% at 8 hrs and 2.6% at 3 days. Figure 2 shows a plot of relative permeation of HD for 8-HQ treated fabric, compared to untreated fabric for multiple sampling for 600 min after spiking.

Table 1. Summary of the results for the reaction of Batch #1 with GD

| **time** | **Untr #1** | **8-HQ #1** | **8-HQ #2** | **8-HQ #3** | **Untr #2** |
|---|---|---|---|---|---|
| 1 day | 7.7 | ND | ND | ND | 5.4 |
| 5 day | 42.6 | 0.6 | 0.37 | 0.34 | 34.5 |

Ave. relative signal (8-HQ/blank) for 5 day results: 1.12%

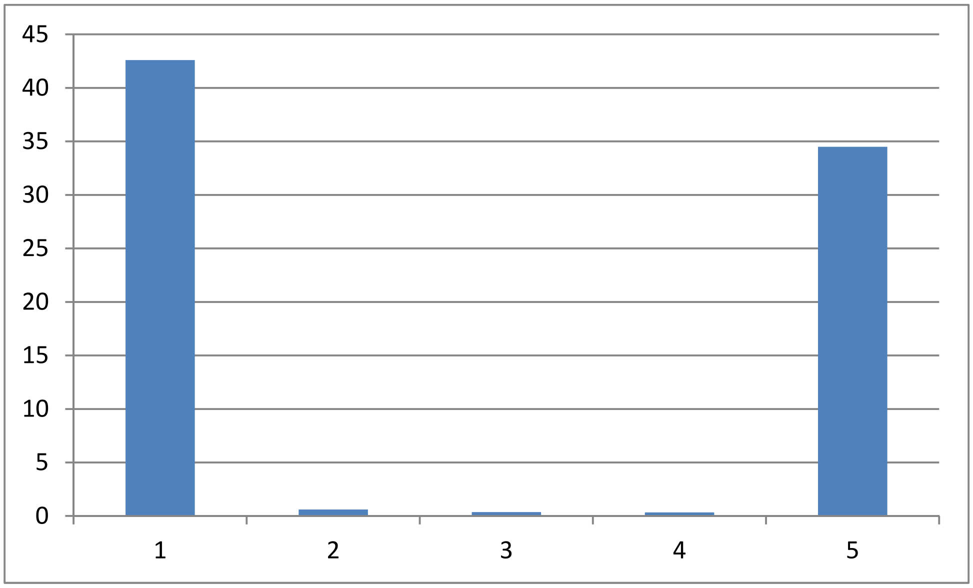



Figure 1. Bar graph of relative GD permeation for 8-HQ treated fabric samples (#2, 3, 4), compared to untreated fabric (#1, 5) after 5 days.

Table 2. Summary of the results for the reaction of 8-HQ Batch #1 with DFP

| **time** | **Untr #1** | **8-HQ #1** | **8-HQ #2** | **8-HQ #3** | **Untr #2** | **Ave (8-HQ/blank)** |
|---|---|---|---|---|---|---|
| 8 hrs | 190.9 | 19.1 | 15.6 | 24.8 | 157.5 | 11.3% |
| 1 day | 244.2 | 14.22 | 12.6 | 16.1 | 256.8 | 5.7% |
| 2 days | 185.2 | 2.8 | 2.8 | 3.8 | 245.1 | 1.4% |

Table 3. Summary of the results for the reaction of 8-HQ Batch #1 with HD

| **time** | **Blank #1** | **8-HQ #1** | **8-HQ #2** | **8-HQ #3** | **Blank #2** | **Ave (8-HQ/blank)** |
|---|---|---|---|---|---|---|
| 8 hrs | 152.4 | 18.4 | 15.6 | 16.1 | 155.5 | 10.7% |
| 3 days | 27.86 | 0.966 | 0.737 | 0.957 | 39.02 | 2.6% |

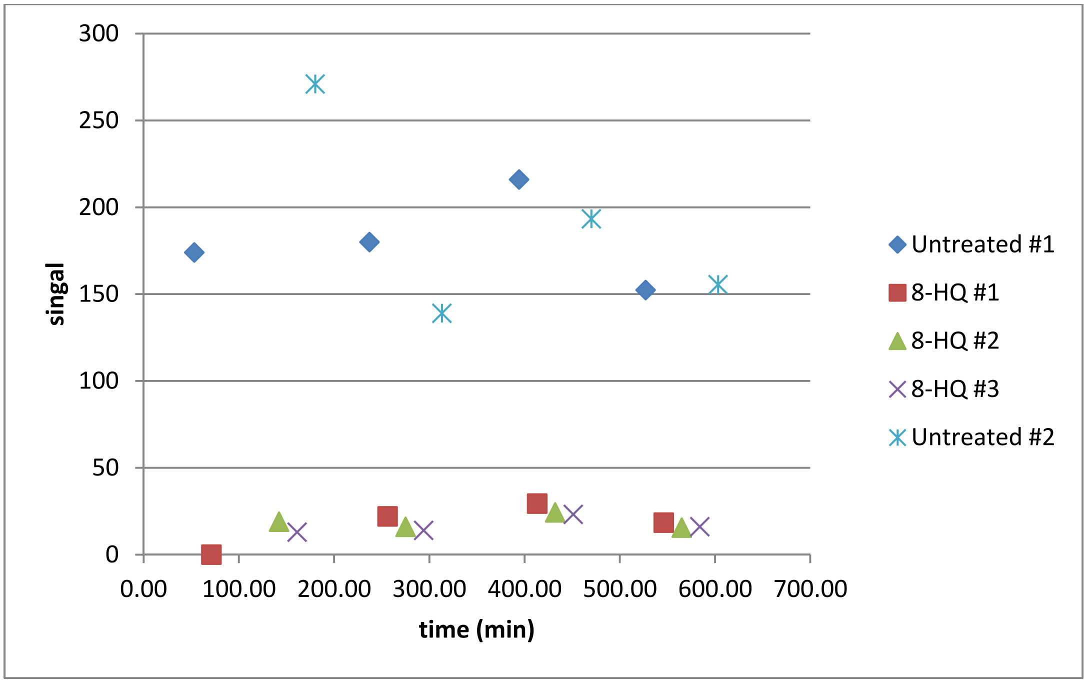



Figure 2. Plot of relative permeation of HD for 8-HQ treated fabric, compared to untreated fabric for multiple sampling for 600 min after spiking.

## 3.2 Liquid Solution Deposition on 8-HQ Fabric

For reactive liquid exposure testing, the dilute agent standard was deposited directly on the fabric to check for reaction. The agent amount was 20 µg per vial, using a 1 mg/mL dilute solution. An inner vial wasn't used. If the fabric is more reactive, the agent signal should be less. 8-HQ treated fabric had lower signal for GD, HD, and DFP compared to untreated fabric, as shown in Table 4. These results indicate that the fabric can be effective against dilute solutions of agent deposited as liquid. However, the results weren't very reproducible on subsequent tests.

Table 4: Results for deposition of dilute agent solution on 8-HQ treated fabric using one untreated fabric sample and 2 treated samples

| agent | untr | 8-HQ #1 | 8-HQ #2 | Ave (8-HQ/blank) |
|---|---|---|---|---|
| GD | 469.2 | 0.94 | 0.4 | 0.14% |
| HD | 4164 | 54.3 | 76.4 | 1.57% |
| DFP | 1543 | 11.9 | 8.3 | 0.65% |

### 3.3 Comparison of 8-HQ Fabric from Different Batches

In April 2012, Batch #2 of 8-HQ fabric was received from Natick. Batch #2 was labeled KMS20120321 from Tyndall AFB (made in March, 2012). Batch #2 was compared directly to Batch #1 for GD reactions using alternating runs using the Headspace GC/MS method. Results are shown in Table 5. Signals for the untreated fabrics are consistent with each other. Signals for 8-HQ Batch #2 are consistently higher than for Batch #1. Averaging the results, the Batch #1 fabric has permeation that is 19.5% of that of the Batch #2 fabric. Bar charts of the results are shown in Figure 3. It is not clear what causes the difference.

Table 5. Summary of the results of the comparison of Batch #1 and Batch #2 using the headspace vial-in-vial method with GD

Batch #1

| Time after spike (min) | Untr. #1 | Untr. #2 | 8-HQ batch 1 #1 | 8-HQ batch 1 #2 |
|---|---|---|---|---|
| 1423 | 1245 | 1335 | 46 | 52 |
| 1637 | 1271 | 1509 | 35 | 36 |
| 3009 | 1031 | 1403 | 16.6 | 13.8 |
| 4235 | 302 | 463 | 7 | 5 |

Batch #2

| Time after spike (min) | Untr. #3 | Untr. #4 | 8-HQ batch 2 #1 | 8-HQ batch 2 #2 |
|---|---|---|---|---|
| 1327 | 751 | 962 | 206 | 140 |
| 1462 | 1194 | 1432 | 210 | 132 |
| 1756 | 1309 | 1516 | 176 | 101 |
| 3089 | 1026 | 1080 | 86.1 | 36.7 |
| 4353 | 410 | 446 | 41.1 | 16.5 |

| time (min) and batch no. | Ave (8-HQ #n/blank) | ratio, batch 1/batch 2 |
|---|---|---|
| 1327 #2 | 20.20% | |
| 1423 #1 | 3.80% | 18.81% |
| 1462 #2 | 13.02% | |
| 1637 #1 | 2.55% | 19.61% |
| 1756 #2 | 9.81% | |
| 3009 #1 | 1.25% | 12.74% |
| 3089 #2 | 5.83% | |
| 4235 #1 | 1.57% | 26.90% |
| 4353 #2 | 6.73% | |
| | average | 19.51% |
| | std. dev. | 5.80% |

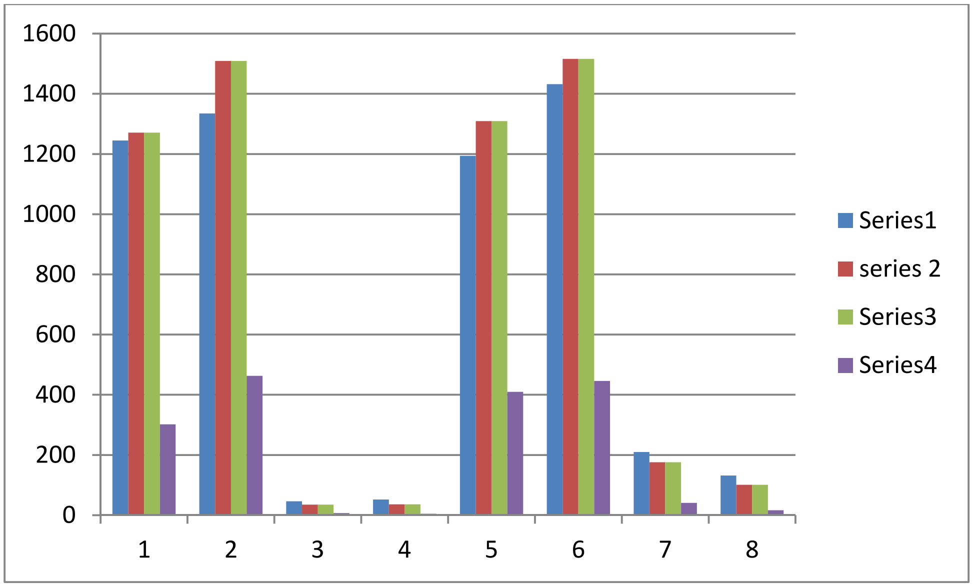



Figure 3. Bar chart of untreated fabric, Batch #1 and Batch #2 results, with each series run in order shown. Data for 1, 2, 5, and 6 are for untreated fabrics; and 3 and 4 are 8-HQ treated Batch #1, and 7 and 8 are from 8-HQ treated Batch #2.

### 3.4 8-HQ/BIT Reactivity on March 2014 Fabrics at Ambient Humidity

A set of samples was made at Tyndall AFB to test reactivity of 8-HQ and BIT additives on cloth. The samples are listed in Table 6, and were produced in March 2014 with a combination of 8-HQ and BIT additives. The previous Batch #1 and Batch #2 are also given, but they were 3 and 2 years old at this time, respectively. These fabrics were all NyCo cover fabrics.

Table 6. Treatment of a set of fabrics from Tyndall AFB

| **Sample Name** | **Description** |
|---|---|
| KMS20140331A | 2% salicylamide |
| KMS20140331B | 2% BIT (benzisothiazolinone) |
| KMS20140331C | 1% BIT, 1% 8-HQ |
| KMS20140331D | 2% 8-HQ (8-hydroxyquinoline) |
| KMS20110719 | Batch #1 Sample with 8-HQ treatment, 2011. |
| KMS20120321 | Batch #2 Sample with 8-HQ treatment, 2012. |

Headspace vial-in-vial tests were done on these samples using agent spikes of HD and GD. The amount of agent used in the inner vial was 25 µg, corresponding to 1 g/m$^2$ of agent dose.

Table 7 shows results for HD on the set of samples, with one repetition each. For HD, sample D is 50% lower than the others, but for the rest there isn't a significant difference between the other untreated fabric and the treated samples. The GD samples are shown in Table 8, and the untreated fabric and samples C and D are about the same, but samples A and B are higher than the untreated fabric,

which is difficult to explain. It appears that the untreated fabric result is anomalously low and the results for samples A is closer to the unreactive value.

Since samples C and D have 8-HQ, the results are consistent with some reactivity for the treatment. But the results do not show as large of an effect from the 8-HQ fabrics compared to the untreated fabrics with the vapor permeation test. The previously tested fabrics were still available, so they were tested again using the same method against HD. The results are shown in Table 9. There wasn't a large effect for these fabrics either, even though they worked well before.

Table 7. HD on new set of Tyndall fabrics using Headspace vial in vial method

| filename | agent | Sample name | Signal |
|---|---|---|---|
| 140509004 | HD | untreated | 31.2 |
| 140509005 | HD | KMS20140331A | 29.6 |
| 140509006 | HD | KMS20140331B | 35.8 |
| 140509007 | HD | KMS20140331C | 30.3 |
| 140509008 | HD | KMS20140331D | 15.5 |
| 140509009 | HD | 20 ug HD std | 60.7 |

Table 8. GD on new set of Tyndall fabrics using Headspace vial in vial method

| filename | agent | Sample name | Signal |
|---|---|---|---|
| 140509026 | GD | untreated | 6.4 |
| 140509027 | GD | KMS20140331A | 53.9 |
| 140509028 | GD | KMS20140331B | 10.75 |
| 140509029 | GD | KMS20140331C | 5.4 |
| 140509030 | GD | KMS20140331D | 4.9 |
| 140509031 | GD | 20 ug GD std | 28.3 |
| 140509032 | GD | blank | nd |

Table 9. HD on old Tyndall fabrics using Headspace vial in vial method

| filename | agent | Sample name | Signal |
|---|---|---|---|
| 140513004 | HD | untr. Cotton #1 | 179 |
| 140513005 | HD | untr. Cotton #2 | 168 |
| 140513006 | HD | KMS20110719 #1 | 153 |
| 140513007 | HD | KMS20110719 #2 | 140 |
| 140513008 | HD | KMS20120321 #1 | 117 |
| 140513009 | HD | KMS20120321 #2 | 106 |

*NMR Results:* Liquids NMR studies of the March 2014 fabric samples were done to show qualitative results and to look for nonvolatile reaction products. Fabrics were spiked with HD or GD and extracted after 24 hrs. using acetonitrile, and the extracts were analyzed. Reaction products were not observed for the HD spikes. For the GD spike, partial reaction is observed. But the highest fraction of reaction products was observed for the untreated fabrics. The results for the NMR method and

headspace GC method are consistent to the extent that neither show large effects of reaction on these treated fabrics.

Table 10. NMR method results for the set of fabrics in Table 6

| **filename** | **agent** | **Sample name** | **Signal** | |
|---|---|---|---|---|
| NB229P90G | HD | untreated | | HD observed, no products |
| NB229P90H | HD | KMS20140331A | | HD observed, no products |
| NB229P90I | HD | KMS20140331B | | HD observed, no products |
| NB229P90J | HD | KMS20140331C | | HD observed, no products |
| NB229P90K | HD | KMS20140331D | | HD observed, no products |
| NB229P90L | GD | untreated | | 83% acid product, 17% GD |
| NB229P90M | GD | KMS20140331A | | 50% acid product, 50% GD |
| NB229P90N | GD | KMS20140331B | | 75% acid product, 25% GD |
| NB229P90O | GD | KMS20140331C | | 70% acid product, 30% GD |
| NB229P90P | GD | KMS20140331D | | 60% acid product, 40% GD |

## 3.5 Effect of Humidity on GD Headspace Vapor

To test the effect of humidity on the reactivity, the Headspace vial-in-vial GC method was used with the following modifications. Spiking was done using dilute solutions of agent (1 mg/ml) in methylene chloride, to allow the solvent to evaporate faster. In order to test the effect of different relative humidities, different water solutions were added to the outer headspace vial of each sample:

1. Pure DI water: 20 µl of liquid water were added to the outer vial. During runs, excess water droplets could be observed in the outer vial indicating that the relative humidity was near 100%.
2. 20 µl of a solution of saturated NaBr solution, which provides a relative humidity of 60%, was added to the outer vial.
3. Ambient humidity air was in the outer vial, with a relative humidity at room temperature of about 30-40% (already discussed in Section 3.4).

For these experiments, the extra water in the outer vial exposes the fabric to a controlled amount of humidity. The CWA in the inner vial may or may not be exposed to excess water before it permeates through the fabric. Of course, the humidity conditions may not be as well controlled in the vials as they are for more complex instrumentation for which the air is conditioned before exposing the fabric.[4]

Fabrics that were tested in this series are given in Table 6, with the additional sample of Sigmaversatech (SVT) fabric, a sample that was treated with omniphobic repellant coating as well as 8-HQ and BIT (see also Section 3.7).

A strong dependence on the humidity was found. At 60% RH, a large suppression of GD headspace vapor was observed for the 8-HQ treated fabrics. For 100% RH, most of the GD was removed

after 48 hrs for all fabrics whether they were treated or not. For 30% RH, little effect was observed for any of the fabrics.

Table 11 shows the repeated runs with three replicate samples of each of the treated fabrics at 60% RH. The data for the overall averages and standard deviations is shown in Figure 4. There is little change in the GD headspace over time, over the three days of rerunning the samples. The sample KMS20140331D has a GD vapor concentration that is 3% (±3% standard deviation) compared to the untreated fabric, which is about the same level as expected from previous experiments with 8-HQ treated fabrics. The sample KMS20140331C, that had half as much 8HQ, has a GD vapor concentration of 9.6% (±5.7% standard deviation).

The SVT fabrics were not significantly different from the untreated fabrics. However, the SVT fabrics were heated to apply the omniphobic coating, and the heat treatment may have evaporated the 8HQ.

Table 11. GD raw data results on 8-HQ/BIT fabrics with 60% RH

| Time started: | 6/10/2014 17:07 | 6/11/2014 0:24 | 6/11/2014 7:41 | 6/11/2014 14:57 | 6/12/2014 9:11 |
|---|---|---|---|---|---|
| **descr.** | **GD, set 1** | **GD, set 2** | **GD set 3** | **GD set 4** | **GD set 5** |
| 30 ug GD | 1191 | | | | 474 |
| untr #1 | 594 | 272 | 291 | 346 | 285 |
| untr #2 | 660 | 377 | 374 | 388 | 289 |
| untr #3 | 632 | 372 | 327 | 291 | 182 |
| SVT #1 | 339 | 317 | 343 | 373 | 318 |
| SVT #2 | 277 | 304 | 355 | 394 | 352 |
| SVT #3 | 282 | 328 | 385 | 402 | 350 |
| 0331B #1 | 268 | 333 | 333 | 305 | 183 |
| 0331B #2 | 189 | 259 | 248 | 216 | 129 |
| 0331B #3 | 212 | 294 | 277 | 227 | 132 |
| 0331C #1 | 56.7 | 79.2 | 72.6 | 59.3 | 30.8 |
| 0331C #2 | 36.9 | 31.7 | 27.6 | 21.6 | 11.7 |
| 0331C #3 | 40.4 | 31.3 | 23.7 | 17.5 | 7.4 |
| 0331D #1 | 18.2 | 4 | 3.7 | 3.6 | 2.1 |
| 0331D #2 | 39 | 23.9 | 30 | 24 | 10.4 |
| 0331D #3 | 0.3 | 2.1 | 3.3 | 3 | 0.6 |
| blank | 0 | 0 | 0 | 0 | 0 |
| 30 ug GD | 559 | 493 | 595 | 607 | 512 |

The outer vial has 20 ul of saturated NaBr solution to make 60% RH. Vials were capped at 6/10/2014 11:50 am, and the start times of the runs are shown at the top of the columns.

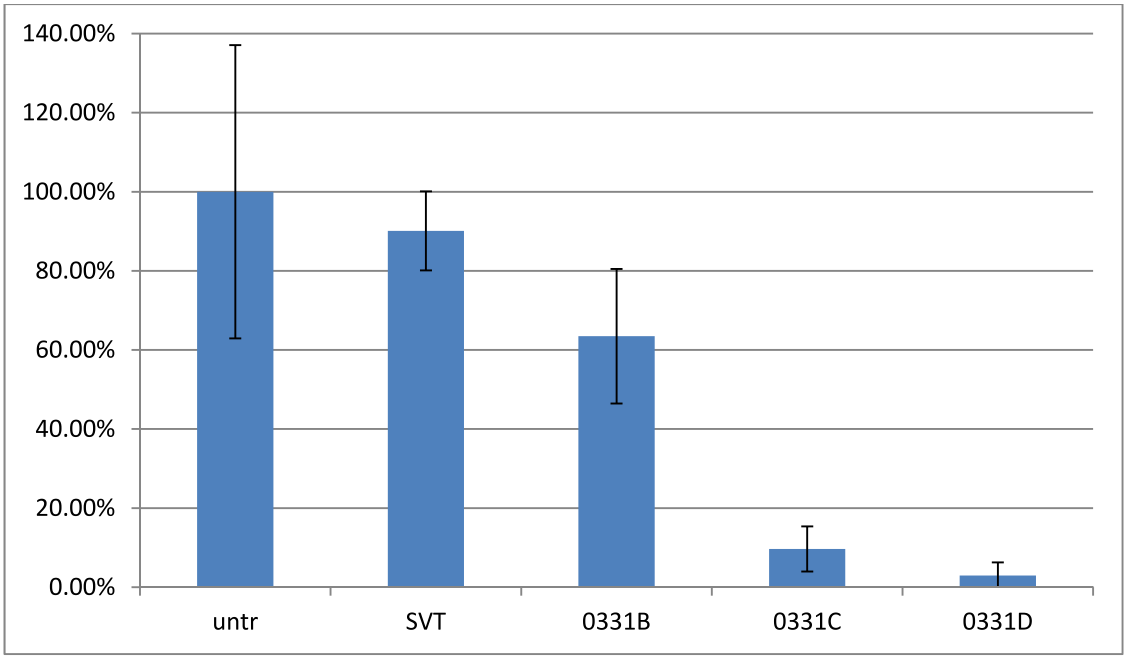



Figure 4. Averaged data from Table 11 for permeation of the fabrics shown at 60% RH, including standard deviation (±1 std. dev. for n = 15) error bars for all 5 sets of data normalized to the untreated fabric data. The higher standard deviation for the untreated fabrics is mostly caused by the higher signals for the set 1 (first repetition) runs.

Table 12 shows two repeated runs of three replicate samples of the treated fabrics at 100% RH. At 6 hrs after spiking, the 0331D samples (with 8HQ) showed low signal of 2% compared to the untreated fabric samples, as shown in Figure 5. By 48 hrs, no GD vapor is detected in any of the samples.

For data set #1, the 2 µg and 20 µg GD standards (without reactive fabric) had 20 µl of water added to the inner vial as well as GD, and the GD in the standard was not observed, indicating that there was enough water to react with the GD even without reactive fabric. For data set #3, new standards were made without water added to the vial for QC purposes, and the GD was observed.

Data for the case with ambient air in the outer headspace vial is shown for HD and GD in Section 3.4. The ambient humidity in the room was not adjusted, but it is 30-40% RH.

Table 12. GD results on 8-HQ/BIT fabrics with 100% RH

| Time started: | 6/4/2014 17:00 | 6/6/2014 16:00 |
|---|---|---|
| **Sample** | **GD, set 1** | **GD, set 3** |
| 2 ug GD | nd | nd |
| 20 ug GD | nd | 121.9 |
| blank | nd | 9.6 |
| untr #1 | 22.8 | 3.2 |
| untr #2 | 36.1 | 0.5 |
| untr #3 | 23 | 0.6 |
| SVT #1 | 44.5 | nd |
| SVT #2 | 37.2 | nd |
| SVT #3 | 23.4 | nd |
| 0331B #1 | 33.1 | nd |
| 0331B #2 | 11.8 | nd |
| 0331B #3 | 16.2 | nd |
| 0331C #1 | 25.7 | nd |
| 0331C #2 | 7.4 | nd |
| 0331C #3 | 4 | nd |
| 0331D #1 | 1.7 | nd |
| 0331D #2 | 0 | nd |
| 0331D #3 | 0 | nd |
| blank | nd | nd |
| 2 ug GD | nd | 0.12 |
| 20 ug GD | 2.1 | 278 |
| blank | nd | 13 |

Outer vial has 20 ul of DI water. Capped at 6/4/2014 at 11:00 am

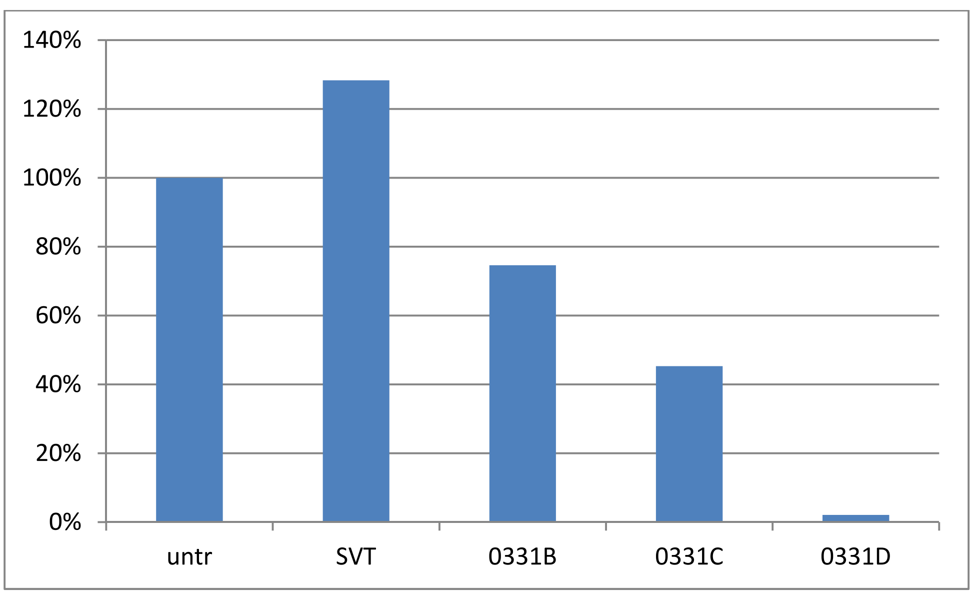



Figure 5. Averaged data from Table 12 for permeation of the fabrics shown at 100% RH after 6 hrs.

## 3.6 Summary of Humidity Variation Results

The summary of the results is shown in Table 13 for all three humidity cases. The results are normalized to the signal for untreated fabric as 100%, except for the case of 30% RH, for which the untreated fabric signal appears to be anomalously low. The 0331D fabric, treated with 2% 8-HQ, has the best performance in all cases, but it performs better at higher relative humidity.

Table 13. Overall averages relative to the untreated fabrics

| **Descr.** | **60% RH[a)]** | **100% RH[b)]** | **30% RH[c)]** |
|---|---|---|---|
| Untreated fabric | 100% ± 37.1% | 100% | 11.9% |
| SVT | 90.1% ± 10.0% RSD | 128.3% | NA |
| 0331A | NA | NA | 100% |
| 0331B | 63.5% ± 17.1% RSD | 74.6% | 19.9% |
| 0331C | 9.6% ± 5.7% RSD | 45.3% | 10.0% |
| 0331D | 3.0% ± 3.3% RSD | 2.1% | 9.1% |

a) Average of 3 replicates and 5 runs (see Table 11) averaged over a time period of 0.5-2 days. Relative Standard Deviation (RSD) values are reported for all values used in the average, relative to the permeation of the untreated fabric reference.
b) Average of 3 replicates, one run each (see Table 12) for a time period of 6-12 hours after spiking. GD was undetected by 48 hrs.
c) One replicate, one run, discussed further in Section 3.4. Normalized to 0331A signal because the untreated fabric appeared to be anomalously low.
NA= Not Analyzed.

The SVT fabrics were not significantly different from the untreated fabrics. However, the SVT fabrics were heated to apply the omniphobic coating, and the heat treatment may have evaporated the 8-HQ. As a result, the 8-HQ manufacturing process will require no heating after the 8-HQ application, to keep it on the fabric. Studies of laundering are also needed to determine whether the chemical will wash off under normal laundry conditions.

Section 3.3 and 3.4 discuss measurements for which the 8-HQ doesn't perform as well as the optimal conditions. The difference appears to be due to low humidity conditions. Since the treated shell fabrics are on the outside of the garment system, it may be more subject to ambient humidity than the inner layers, which are humidified by the wearer. As a result, it is possible that the performance of the outer shell layer may be more variable than would be desirable. However, if 8-HQ is applied to the inner layers, it may work as expected.

There isn't evidence that the BIT treatment provides additional reactivity. However, BIT may still be important as a biocidal compound, even if no chemical activity is provided.

The mechanism of the 8-HQ reactivity still needs study to try other experimental methods to study the reactions involved, in order to determine whether the CWA is adsorbed or reacted.

## 3.7 Effect of Repellency Treatment

A further improvement on the outer shell fabric was to add an omniphobic repellency coating that should improve the shedding of liquids. This coating would make the outer fabric rain and water resistant, and it would also improve shedding of drops of liquid CWA. A study was done to see whether the addition of the repellent coating would affect the performance of the 8-HQ/BIT treatment.

A set of samples labeled KMS130208 were analyzed by headspace GC for permeation of agent though the fabric. The set of sample was prepared at Tyndall AFB and sent to ECBC by Heidi Gibson in May 2013. Five pairs of samples (labeled A to E) are in the set that are identical replicates. A control untreated sample KMS130208G was also received. One sample in each pair is treated with reactive 8-HQ and BIT treatment but no repellency treatment. The other sample in each pair has the same reactive treatment and in addition LUNA repellent treatment. Fabrics are brown colored NyCo fabric (not camouflage colored). Analysis was completed by July 11, 2013.

The summary of the results indicates that there was higher permeation through the repellent-treated fabrics than for the fabric with no repellent treatment. The amount of permeation was referenced to the amount of the headspace concentration of agent, compared to the permeation through untreated fabric. The non-repellent fabric permeation was in the range of 0% (undetectable permeation) to 2% relative to untreated control fabrics, for GD. The repellent fabric had more permeation than the non-repellent fabric but less permeation than untreated control fabric, in the range of 18-31% as much for GD. There was more permeation for HD than GD, and less difference between the non-repellent and repellent fabrics.

Two replicates of each fabric sample were tested for GD or HD permeation using the Headspace GC method. The Headspace vial-in-vial GC method was used as described with the following slight variation, including using the headspace vial size of 20 ml (from previously using 10 ml) and using aluminum crimp caps on the inner vials (instead of plastic snap caps). These changes were based on experience with the method. The Headspace GC analytical method for fabric permeation used a Varian CP-3800 GC instrument with CombiPAL autosampler. It has slight modifications from an older version of the method that was done using an Agilent GC/MS with a Gerstel MPS-2 autosampler, only because the instrument was no longer available for use on this project.

A quantity of 50 µg of GD or HD (50 µl of a 1 mg/ml solution for GD, or 10 µl of a 5 mg/ml solution for HD) was deposited in the small 1-ml vial. The solvent was allowed to evaporate for 15 min. A circle of the test fabric 5/16” in diameter is cut using a Universal hole punch and placed in an aluminum crimp cap that fits the inner vial. Two replicates of each fabric sample were prepared. Each one was analyzed multiple times over time from 1 to 5 days to look for time-dependent permeation.

For the GD runs, the replicates were prepared in two batches. The first batch was for fabrics KMS130208A (2 replicates), B (2 replicates) and C (1 replicate); and the second batch for fabrics KMS130208C (1 replicate), D (2 replicates), and E (2 replicates). Each sample letter consists of non-repellent and repellent fabrics, for a total of 10 samples per batch. Two replicates of KMS130208G (untreated control fabric) were analyzed in each batch as references to determine permeation of untreated fabric.

*Exposure dose of agent on the fabric:* Using the 50-µg dose of agent and 6 mm diameter of exposed fabric, the area is 0.283 $cm^2$, and the dose is 50 µg/0.283 $cm^2$ = 2 $g/m^2$.

Fabrics were stored at ambient humidity of about 50% RH. Reactivity of the fabrics may depend on the humidification, but the study of the effects of humidity wasn't done for this set of experiments.

For GD, the pulsed FPD was operated in conditions that were recommended for phosphorus detection, using a phosphorus filter and a data collection window of 4-10 msec. The phosphorus calibration is linear. The injection port was held at 60°C during the injection to trap the analyte during the gas injection using a 5:1 split, and then the injector port was rapidly heated to 200°C to desorb the analyte to the column. Even with these conditions, greater sensitivity would have been helpful for some of the runs. It is possible that the sensitivity could be improved by optimizing the flow of the flame gases to the FPD, but the default recommended settings were used.

For HD, the pulsed FPD was operated using conditions for sulfur detection, using a sulfur filter and data collection window of 6-20 msec. The calibration for sulfur has a quadratic calibration curve. The pulsed FPD was more sensitive to S than P. In order to obtain appropriate signal response, it was necessary to use a hot injection port (200°C) and a 100:1 split in the injection port. As a result of these effects, more thorough studies of the calibration for S were done. Calibration was done both using standards prepared in headspace vials and in liquid solutions, using the same detector conditions.

*GD data:* The data for runs of the entire set of samples is shown in Table 14. The column under "area" is the raw integrated area of the GC peak in arbitrary units, and "ref. untr." is the comparison signal for two untreated fabric runs as a reference for normalization. This data is provided in case there is a need for statistical analysis of the multiple reps and runs for this sample set. The dates, times, and filenames for the runs are also shown. The signals for the untreated fabrics from 19-Jun appear anomalously low at 30.5 and 16.6, so it may be preferable to exclude the data from this day since they make the normalized results high. The average signal and standard deviation are given for the combined runs for each fabric sample. Correcting the signals by normalizing relative to the untreated samples before averaging did not improve the relative standard deviation.

Table 14. Raw data results for Headspace GC permeation tests for GD. Samples for A, B and C (rep.1) were prepared on 19-Jun at 10:45 am. Samples for C (rep. 2), D, and E were prepared on 24-Jun at 10:10 am.

| fabric | no repell / repell | file | area | date | time | ref. untr. 1 | ref. untr. 2 |
|---|---|---|---|---|---|---|---|
| KMS20130208A | no rep. 1 | 130619a003 | 0 | 19-Jun | 18:36 | 30.5 | 16.6 |
| (2 samples each, rerun 3 times) | no rep. 2 | 130619a004 | 10.7 | | 19:24 | 30.5 | 16.6 |
| | no rep. 1 | 130621003 | 3.6 | 21-Jun | 11:53 | 232 | 213 |
| | no rep. 2 | 130621004 | 0 | | 12:41 | 232 | 213 |
| | no rep. 1 | 130621016 | 2 | 21-Jun | 22:19 | 242 | 200 |
| | no rep. 2 | 130621017 | 0 | | 23:07 | 242 | 200 |
| | average | | 2.72 | | | | |
| | std. dev. | | 4.18 | | | | |
| KMS20130208A | rep. 1 | 130619a005 | 12.7 | 19-Jun | 20:12 | 30.5 | 16.6 |
| (2 samples each) | rep. 2 | 130619a006 | 10.5 | | 21:01 | 30.5 | 16.6 |
| | rep. 1 | 130621005 | 1.05 | 21-Jun | 13:29 | 232 | 213 |
| | rep. 2 | 130621006 | 37.6 | | 14:17 | 232 | 213 |
| | rep. 1 | 130621018 | 1.9 | 21-Jun | 23:55 | 242 | 200 |
| | rep. 2 | 130621019 | 29.8 | 22-Jun | 0:43 | 242 | 200 |
| | average | | 15.59 | | | | |
| | std. dev. | | 14.96 | | | | |
| KMS20130208B | no rep. 1 | 130619a007 | 0 | 19-Jun | 21:49 | 30.5 | 16.6 |
| (2 samples each) | no rep. 2 | 130619a008 | 0 | | 22:24 | 30.5 | 16.6 |
| | no rep. 1 | 130621007 | 7.3 | 21-Jun | 15:05 | 232 | 213 |
| | no rep. 2 | 130621008 | 8.9 | | 15:54 | 232 | 213 |
| | no rep. 1 | 130621020 | 3.25 | 22-Jun | 1:31 | 242 | 200 |
| | no rep. 2 | 130621021 | 6.6 | | 2:19 | 242 | 200 |
| | average | | 4.34 | | | | |
| | std. dev. | | 3.83 | | | | |
| KMS20130208B | rep. 1 | 130619a009 | 42.6 | 19-Jun | 23:12 | 30.5 | 16.6 |
| (2 samples each) | rep. 2 | 130619a010 | 9.5 | 20-Jun | 0:13 | 30.5 | 16.6 |
| | rep. 1 | 130621009 | 34.1 | 21-Jun | 16:42 | 232 | 213 |
| | rep. 2 | 130621010 | 50.1 | | 17:30 | 232 | 213 |
| | rep. 1 | 130621022 | 27.6 | 22-Jun | 3:08 | 242 | 200 |
| | rep. 2 | 130621023 | 44.8 | | 3:56 | 242 | 200 |
| | average | | 34.78 | | | | |
| | std. dev. | | 14.75 | | | | |
| KMS20130208C | no rep. 1 | 130619a011 | 26.1 | 20-Jun | 1:01 | 30.5 | 16.6 |
| (2 samples each) | no rep. 1 | 130621011 | 2.3 | 21-Jun | 18:18 | 232 | 213 |
| | no rep. 1 | 130621024 | 0.6 | 22-Jun | 4:44 | 242 | 200 |
| | no rep. 2 | 130625003 | 0 | 25-Jun | 11:45 | 209 | 131.3 |
| | no rep. 2 | 130625017 | 1.5 | 25-Jun | 22:48 | 451 | 385 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | no rep. 2 | 130626003 | 0 | 26-Jun | 11:26 | 598 | 561 |
| | no rep. 2 | 130627003 | 0 | 27-Jun | 11:28 | 535 | 400 |
| | average | | 4.36 | | | | |
| | std. dev. | | 9.63 | | | | |
| KMS20130208C | rep. 1 | 130619a012 | 101.1 | 20-Jun | 1:49 | 30.5 | 16.6 |
| (2 samples each) | rep. 1 | 130621012 | 31.3 | 21-Jun | 19:06 | 232 | 213 |
| | rep. 1 | 130621025 | 24.9 | 22-Jun | 5:32 | 242 | 200 |
| | rep. 2 | 130625004 | 74.9 | 25-Jun | 12:33 | 209 | 131.3 |
| | rep. 2 | 130625018 | 65 | 25-Jun | 23:37 | 451 | 385 |
| | rep. 2 | 130626004 | 61.9 | 26-Jun | 12:14 | 598 | 561 |
| | rep. 2 | 130627004 | 71.9 | 27-Jun | 12:16 | 535 | 400 |
| | average | | 61.57 | | | | |
| | std. dev. | | 26.20 | | | | |
| KMS20130208D | no rep. 1 | 130625005 | 0 | 25-Jun | 13:21 | 209 | 131.3 |
| (2 samples each, rerun 4 times) | no rep. 2 | 130625006 | 5.5 | 25-Jun | 14:09 | 209 | 131.3 |
| | no rep. 1 | 130625019 | 0 | 26-Jun | 0:25 | 451 | 385 |
| | no rep. 2 | 130625020 | 0 | 26-Jun | 1:13 | 451 | 385 |
| | no rep. 1 | 130626005 | 0 | 26-Jun | 13:02 | 598 | 561 |
| | no rep. 2 | 130626006 | 0 | 26-Jun | 13:50 | 598 | 561 |
| | no rep. 1 | 130627005 | 0 | 27-Jun | 13:04 | 535 | 400 |
| | no rep. 2 | 130627006 | 0 | 27-Jun | 13:53 | 535 | 400 |
| | average | | 0.69 | | | | |
| | std. dev. | | 1.94 | | | | |
| KMS20130208D | rep. 1 | 130625007 | 78.9 | 25-Jun | 14:57 | 209 | 131.3 |
| (2 samples each) | rep. 2 | 130625008 | 117.6 | 25-Jun | 15:46 | 209 | 131.3 |
| | rep. 1 | 130625021 | 48.2 | 26-Jun | 2:01 | 451 | 385 |
| | rep. 2 | 130625022 | 81.7 | 26-Jun | 2:49 | 451 | 385 |
| | rep. 1 | 130626007 | 41.4 | 26-Jun | 14:39 | 598 | 561 |
| | rep. 2 | 130626008 | 86.6 | 26-Jun | 15:27 | 598 | 561 |
| | rep. 1 | 130627007 | 39.15 | 27-Jun | 14:41 | 535 | 400 |
| | rep. 2 | 130627008 | 80.2 | 27-Jun | 15:29 | 535 | 400 |
| | average | | 71.72 | | | | |
| | std. dev. | | 26.95 | | | | |
| KMS20130208E | no rep. 1 | 130625009 | 0 | 25-Jun | 16:34 | 209 | 131.3 |
| (2 samples each) | no rep. 2 | 130625010 | 0 | 25-Jun | 17:12 | 209 | 131.3 |
| | no rep. 1 | 130625023 | 0 | 26-Jun | 3:37 | 451 | 385 |
| | no rep. 2 | 130625024 | 0 | 26-Jun | 4:25 | 451 | 385 |
| | no rep. 1 | 130626009 | 0 | 26-Jun | 16:15 | 598 | 561 |
| | no rep. 2 | 130626010 | 0 | 26-Jun | 17:03 | 598 | 561 |
| | no rep. 1 | 130627009 | 0 | 27-Jun | 16:17 | 535 | 400 |
| | no rep. 2 | 130627010 | 0 | 27-Jun | 17:05 | 535 | 400 |
| | average | | 0.00 | | | | |
| | std. dev. | | 0.00 | | | | |
| KMS20130208E | rep. 1 | 130625011 | 136.6 | 25-Jun | 18:00 | 209 | 131.3 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| (2 samples each) | rep. 2 | 130625012 | 107 | 25-Jun | 18:48 | 209 | 131.3 |
| | rep. 1 | 130625025 | 90.3 | 26-Jun | 5:14 | 451 | 385 |
| | rep. 2 | 130625026 | 68.7 | 26-Jun | 6:02 | 451 | 385 |
| | rep. 1 | 130626011 | 95.2 | 26-Jun | 17:51 | 598 | 561 |
| | rep. 2 | 130626012 | 71.6 | 26-Jun | 18:39 | 598 | 561 |
| | rep. 1 | 130627011 | 102.8 | 27-Jun | 17:54 | 535 | 400 |
| | rep. 2 | 130627012 | 76.1 | 27-Jun | 18:42 | 535 | 400 |
| | average | | 93.54 | | | | |
| | std. dev. | | 22.48 | | | | |

Table 15 consolidates the processed data for each fabric sample. It includes the average signal and standard deviation from Table 14, as well as the ratio of the average signal to the average signal of the untreated fabrics. The untreated fabric signal is used as a reference.

Both types of treated fabrics have lower signal than the untreated fabric, implying that the permeation through the fabrics are lower. However, the repellent fabric is higher than the non-repellent fabric. From the range of ratios, the repellent fabric is 18.5 to 31.0% as permeable as the untreated fabric. The non-repellent fabric is in the range of 0% (undetectable) to 2%, compared to the untreated fabric. The undetectable signal level is estimated to be 0.2% or less, and it is the level at which the software integrator will not find the peak. For both fabric sample D and E, the signal for the non-repellent fabric was in the undetectable range.

Table 15. 8-HQ treated with and without repellent treated fabric permeation results. Processed data, average signals for all repetitions, and ratio to untreated control fabric results for Headspace GC permeation tests for GD.

| Fabric | | Signal, all reps. | Ratio to untr. control fabric |
|---|---|---|---|
| KMS20130208A | average | 2.72 | 0.505% |
| no repell | std. dev. | 4.18 | |
| KMS20130208A | average | 15.59 | 21.705% |
| repell | std. dev. | 14.96 | |
| | Ratio, no repell to repell. | 17.42% | |
| KMS20130208B | average | 4.34 | 1.956% |
| no repell | std. dev. | 3.83 | |
| KMS20130208B | average | 34.78 | 22.189% |
| repell | std. dev. | 14.75 | |
| | Ratio, no repell to repell | 12.48% | |
| KMS20130208C | average | 4.36 | 0.277% |
| no repell | std. dev. | 9.63 | |
| KMS20130208C | average | 61.57 | 18.494% |
| repell | std. dev. | 26.20 | |
| | Ratio, no repell to repell | 15.63% | |
| KMS20130208D | average | 0.69 | 0.404% |
| no repell | std. dev. | 1.94 | |
| KMS20130208D | average | 71.72 | 24.273% |
| repell | std. dev. | 26.95 | |
| | Ratio, no repell to repell | 0.96% | |
| KMS20130208E | average | 0.00 | 0.000% |
| no repell | std. dev. | 0.00 | |
| KMS20130208E | average | 93.54 | 31.032% |
| repell | std. dev. | 22.48 | |
| | Ratio, no repell to repell. | 0% | |

*HD Calibration Studies:* In previous studies, it was common that concentration of analyte in headspace vials decreases steadily over time, even with nothing in the vial except the agent that is present as a calibration standard. The decrease was attributed to escaping through the punctured septum, or to absorption of the analyte into the polymer of the septum. Efforts to calibrate the HD signal in this study also found this effect. There is a decrease in signal over time, but it isn't reproducible enough from different vials to calibrate quantitatively. This effect makes it difficult to establish a reliable method for calibration when the standards are in headspace vials, even including the time dependence.

As a result, calibration standards in liquid solution were used. Standards were prepared by diluting the HD stock solution used for spiking in a solution of carbon tetrachloride. A 1-µl solution of the standards was injected using a liquid injection. The same injection port, GC, and detector conditions were used as for the headspace injection, including the 100:1 split flow, but using a different syringe. The plot of calibration was taken over 2 days, and had $R^2$=0.93, n=15, for calibration from 0 to 100 ng, when plotting the square root of signal. Some literature reports have higher values for $R^2$ for a Varian instrument.[5,6] The present data has a better correlation coefficient ($R^2$=0.98) if data for only one day is included. However, the calibration results from liquid injections didn't have a good agreement with the headspace standards, due to the previously discussed time dependence of the signal from headspace standard vials. As a result, it was not possible to obtain quantitative permeation results of HD through the treated fabrics for this data set. More work is needed to determine an accurate calibration method, perhaps with a more accurate detector.

*HD Data for relative permeation of fabrics*: The data for several runs of an entire set of samples is shown in Table 16. One set of samples of each fabric type was rerun repeatedly over 4 days. The column under "area" is the integrated area of the GC peak. The column "calc. amt." is the calculated amount of agent in the outer vial, calibrated using the liquid injection calibration curve. Another set of samples was prepared and run, and the results are qualitatively consistent with this set, but the PFPD signal was close to being saturated for many of the runs, so the quantitative results are unreliable.

The data is process differently from the GD data. For the GD data, the average of the signals was calculated and then the ratio was taken. For HD, the ratio was done first. This was because there was less difference between the non-repellent and repellent fabrics. In addition, in the previous preliminary results, a time dependence was observed for the HD data, and the averaging of the signal would not have shown time dependence.

The dates, times, and time after preparation for the runs are shown. The signals for two samples of untreated reference fabrics are shown in the same row with each sample. The ratio of the signal for the treated fabric to the two untreated fabrics is shown in the third to the right column. For the non-repellent fabric samples, the ratio is in the range of 0.21 to 0.24, so the non-repellent treated fabric has less permeation than the untreated fabric. For the repellent fabric, the ratio is 0.48 to 0.73, so the permeation was still less than the untreated fabric, but more than the non-repellent fabric. This ratio is not as good as that indicated by previous data.

The two right columns show the ratio of non-repellent to repellent fabrics for the signal area and the calculated amount. The ratio of signal is in the range of 0.25 to 0.34. Some of the fabrics may have small time dependence. For example, fabric 130208A shows a decrease from 0.58 at 7 hrs to 0.18 at 53 hrs. Fabrics D and E don't show any trend. The last column shows that the ratio for the

amount of analyte rather than the signal. It is larger due to the square root dependence of the calibration. These ratios are in the range of 0.49 to 0.57, except for Fabric C which is 0.94.

In conclusion,

1. GD shows a significant difference between the untreated fabric reference and the treated fabrics. The non-repellent fabrics have the lowest permeation, and the repellent fabrics are higher, but still lower than the untreated fabrics. Since the GD response on the FPD detector is linear, the ratio can be obtained by taking the ratio of the signals.
2. HD shows less difference between untreated, non-repellent, and repellent fabrics, although the non-repellent fabric still has the lowest permeation. The FPD detector is not linear, so the signal has to be converted to amount in order to take the ratio.
3. The GD results are consistent with the previous study, but the HD results are not as good as the previous study.
4. These samples weren't prepared with good control of the humidity, so low humidity could have contributed to the low reactivity. It is also possible that the repellent-treated fabric has less ability to absorb water, contributing to its lower activity.

Table 16: Raw data results for Headspace GC permeation tests for HD

| fabric | date ran | time elapsed (hr) | area | calc. amt. (ug) | ref. untr. fabric 1 | ref. untr. fabric 2 | signal rel to untr. | signal no rep/rep | conc. no rep/rep |
|---|---|---|---|---|---|---|---|---|---|
| KMS20130208A | 7/22/13 18:00 | 6.67 | 21.4 | 5.01 | 54.9 | 78.2 | 0.32 | | |
| no repell | 7/22/13 23:40 | 12.33 | 39.1 | 6.77 | 95.7 | 132 | 0.34 | | |
| | 7/23/13 13:00 | 25.67 | 14.6 | 4.14 | 143 | 123 | 0.11 | | |
| | 7/23/13 18:20 | 31.00 | 8.14 | 3.09 | 91.8 | 75.5 | 0.10 | | |
| | 7/24/13 16:00 | 52.67 | 2.03 | 1.54 | 23.2 | 13.2 | 0.11 | | |
| | 7/24/13 21:20 | 58.00 | 1.75 | 1.43 | 19.5 | 11.6 | 0.11 | | |
| | 7/25/13 16:00 | 76.67 | 0.76 | 0.94 | 8.05 | 4.83 | 0.12 | | |
| Average | | | | | | | 0.17 | | |
| KMS20130208A | 7/22/13 18:20 | 7.00 | 37.2 | 6.60 | 54.9 | 78.2 | 0.56 | 0.58 | 0.76 |
| repell | 7/23/13 0:00 | 12.67 | 69.9 | 9.05 | 95.7 | 132 | 0.61 | 0.56 | 0.75 |
| | 7/23/13 13:20 | 26.00 | 49.9 | 7.65 | 143 | 123 | 0.38 | 0.29 | 0.54 |
| | 7/23/13 18:40 | 31.33 | 36.3 | 6.52 | 91.8 | 75.5 | 0.43 | 0.22 | 0.47 |
| | 7/24/13 16:20 | 53.00 | 11.3 | 3.64 | 11.8 | 13.5 | 0.89 | 0.18 | 0.42 |
| | 7/24/13 21:40 | 58.33 | 9.75 | 3.38 | 19.5 | 11.6 | 0.63 | 0.18 | 0.42 |
| | 7/25/13 16:20 | 77 | 4.8 | 2.37 | 8.05 | 4.83 | 0.75 | 0.16 | 0.40 |
| Average | | | | | | | 0.61 | 0.31 | 0.54 |
| KMS20130208B | 7/22/13 18:40 | 7.33 | 14.8 | 4.16 | 54.9 | 78.2 | 0.22 | | |
| no repell | 7/23/13 0:20 | 13.00 | 25.7 | 5.49 | 95.7 | 132 | 0.23 | | |
| | 7/23/13 13:40 | 26.33 | 6.79 | 2.82 | 143 | 123 | 0.05 | | |
| | 7/23/13 19:00 | 31.67 | 4.57 | 2.31 | 91.8 | 75.5 | 0.05 | | |
| | 7/24/13 16:40 | 53.33 | 1.47 | 1.31 | 11.8 | 13.5 | 0.12 | | |
| | 7/24/13 22:00 | 58.67 | 1.36 | 1.26 | 19.5 | 11.6 | 0.09 | | |
| | 7/25/13 16:40 | 77.33 | 0.71 | 0.91 | 8.05 | 4.83 | 0.11 | | |
| Average | | | | | | | 0.12 | | |
| KMS20130208B | 7/22/13 19:00 | 7.67 | 40.1 | 6.85 | 54.9 | 78.2 | 0.60 | 0.37 | 0.61 |
| repell | 7/23/13 0:40 | 13.33 | 59.5 | 8.35 | 95.7 | 132 | 0.52 | 0.43 | 0.66 |
| | 7/23/13 14:00 | 26.67 | 41.8 | 7.00 | 143 | 123 | 0.31 | 0.16 | 0.40 |
| | 7/23/13 19:20 | 32.00 | 28.2 | 5.75 | 91.8 | 75.5 | 0.34 | 0.16 | 0.40 |
| | 7/24/13 17:00 | 53.67 | 8.36 | 3.13 | 11.8 | 13.5 | 0.66 | 0.18 | 0.42 |
| | 7/24/13 22:20 | 59.00 | 6.97 | 2.86 | 19.5 | 11.6 | 0.45 | 0.20 | 0.44 |
| | 7/25/13 17:00 | 77.67 | 3.34 | 1.98 | 8.05 | 4.83 | 0.52 | 0.21 | 0.46 |
| Average | | | | | | | 0.49 | 0.24 | 0.48 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| KMS20130208C | 7/22/13 19:40 | 8.33 | 32.2 | 6.14 | 54.9 | 78.2 | 0.48 | | |
| no repell | 7/23/13 1:20 | 14.00 | 49.4 | 7.61 | 95.7 | 132 | 0.43 | | |
| | 7/23/13 14:40 | 27.33 | 9.96 | 3.42 | 143 | 123 | 0.07 | | |
| | 7/23/13 20:00 | 32.67 | 6.02 | 2.66 | 91.8 | 75.5 | 0.07 | | |
| | 7/24/13 17:40 | 54.33 | 1.56 | 1.35 | 11.8 | 13.5 | 0.12 | | |
| | 7/24/13 23:00 | 59.67 | 1.28 | 1.22 | 19.5 | 11.6 | 0.08 | | |
| | 7/25/13 17:40 | 78.33 | 0.61 | 0.85 | 8.05 | 4.83 | 0.09 | | |
| Average | | | | | | | 0.19 | | |
| | | | | | | | | | |
| KMS20130208C | 7/22/13 19:20 | 8.00 | 58.6 | 8.28 | 54.9 | 78.2 | 0.88 | 0.55 | 0.74 |
| repell | 7/23/13 1:00 | 13.67 | 70.8 | 9.11 | 95.7 | 132 | 0.62 | 0.70 | 0.84 |
| | 7/23/13 14:20 | 27.00 | 46.2 | 7.36 | 143 | 123 | 0.35 | 0.22 | 0.83 |
| | 7/23/13 19:40 | 32.33 | 30.5 | 5.98 | 91.8 | 75.5 | 0.36 | 0.20 | 1.27 |
| | 7/24/13 17:20 | 54.00 | 8.71 | 3.19 | 11.8 | 13.5 | 0.69 | 0.18 | 1.07 |
| | 7/24/13 22:40 | 59.33 | 7.22 | 2.91 | 19.5 | 11.6 | 0.46 | 0.18 | 0.91 |
| | 7/25/13 17:20 | 78 | 3.11 | 1.91 | 8.05 | 4.83 | 0.48 | 0.20 | 0.44 |
| Average | | | | | | | 0.55 | 0.32 | 0.54 |
| | | | | | | | | | |
| KMS20130208D | 7/22/13 20:00 | 8.67 | 22.3 | 5.11 | 54.9 | 78.2 | 0.34 | | |
| no repell | 7/23/13 1:40 | 14.33 | 36.7 | 6.56 | 95.7 | 132 | 0.32 | | |
| | 7/23/13 15:00 | 27.67 | 11.9 | 3.73 | 143 | 123 | 0.09 | | |
| | 7/23/13 20:20 | 33.00 | 8.2 | 3.10 | 91.8 | 75.5 | 0.10 | | |
| | 7/24/13 18:00 | 54.67 | 2.92 | 1.85 | 11.8 | 13.5 | 0.23 | | |
| | 7/24/13 23:20 | 60.00 | 2.64 | 1.76 | 19.5 | 11.6 | 0.17 | | |
| | 7/25/13 18:00 | 78.67 | 1.41 | 1.29 | 8.05 | 4.83 | 0.22 | | |
| Average | | | | | | | 0.21 | | |
| | | | | | | | | | |
| KMS20130208D | 7/22/13 20:20 | 9.00 | 67.8 | 8.91 | 54.9 | 78.2 | 1.02 | 0.33 | 0.57 |
| repell | 7/23/13 2:00 | 14.67 | 96.2 | 10.61 | 95.7 | 132 | 0.84 | 0.38 | 0.62 |
| | 7/23/13 15:20 | 28.00 | 52.3 | 7.83 | 143 | 123 | 0.39 | 0.23 | 0.48 |
| | 7/23/13 20:40 | 33.33 | 33.4 | 6.25 | 91.8 | 75.5 | 0.40 | 0.25 | 0.50 |
| | 7/24/13 18:20 | 55.00 | 8.64 | 3.18 | 11.8 | 13.5 | 0.68 | 0.34 | 0.58 |
| | 7/24/13 23:40 | 60.33 | 7.39 | 2.94 | 19.5 | 11.6 | 0.48 | 0.36 | 0.60 |
| | 7/25/13 18:20 | 79 | 3.66 | 2.07 | 8.05 | 4.83 | 0.57 | 0.39 | 0.62 |
| Average | | | | | | | 0.63 | 0.32 | 0.57 |
| | | | | | | | | | |
| KMS20130208E | 7/22/13 20:40 | 9.33 | 28.3 | 5.76 | 54.9 | 78.2 | 0.43 | | |
| no repell | 7/23/13 2:20 | 15.00 | 51.3 | 7.75 | 95.7 | 132 | 0.45 | | |
| | 7/23/13 15:40 | 28.33 | 13 | 3.90 | 143 | 123 | 0.10 | | |
| | 7/23/13 21:00 | 33.67 | 8.61 | 3.18 | 91.8 | 75.5 | 0.10 | | |
| | 7/24/13 18:40 | 55.33 | 2.55 | 1.73 | 11.8 | 13.5 | 0.20 | | |
| | 7/25/13 0:00 | 60.67 | 2.19 | 1.60 | 19.5 | 11.6 | 0.14 | | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 7/25/13 18:40 | 79.33 | 1 | 1.08 | 8.05 | 4.83 | 0.16 | | |
| Average | | | | | | | 0.22 | | |
| | | | | | | | | | |
| KMS20130208E | 7/22/13 21:00 | 9.67 | 107 | 11.19 | 54.9 | 78.2 | 1.61 | 0.26 | 0.51 |
| repell | 7/23/13 2:40 | 15.33 | 117 | 11.71 | 95.7 | 132 | 1.03 | 0.44 | 0.66 |
| | 7/23/13 16:00 | 28.67 | 41.9 | 7.01 | 143 | 123 | 0.32 | 0.31 | 0.56 |
| | 7/23/13 21:20 | 34.00 | 28.9 | 5.82 | 91.8 | 75.5 | 0.35 | 0.30 | 0.55 |
| | 7/24/13 19:00 | 55.67 | 8.4 | 3.14 | 11.8 | 13.5 | 0.66 | 0.30 | 0.55 |
| | 7/25/13 0:20 | 61.00 | 6.62 | 2.78 | 19.5 | 11.6 | 0.43 | 0.33 | 0.58 |
| | 7/25/13 19:00 | 79.67 | 3.03 | 1.88 | 8.05 | 4.83 | 0.47 | 0.33 | 0.57 |
| | | | | | | | 0.69 | 0.33 | 0.57 |

3.8 ePTFE-Based Films

Samples of 8-HQ treated films were received in June 2013. The sample preparation conditions are given in Table 17 for the expanded PTFE (ePTFE) samples made at Tyndall.

Table 17. Sample description of 8-HQ and BIT treated ePFTE films

| Sample Name | Sample Description | TMOS | FSi | 8-HQ | BIT | Microwave | Thermal |
|---|---|---|---|---|---|---|---|
| KMS20130509A | Blank | 0 | 0 | 0.0% | 0.0% | 3 replicates | |
| KMS20130509D | 8-HQ MW'd | 2% | | 1.5% | | 3 replicates | |
| KMS20130509E | 8-HQ thermal | 2% | | 1.5% | | | 3 replicates |
| KMS20130509F | BIT MW'd | 2% | | | 1.5% | 3 replicates | |
| KMS20130509G | BIT thermal | 2% | | | 1.5% | | 3 replicates |
| KMS20130509H | 8-HQ and BIT MW'd | 2% | | 1.5% | 1.5% | 3 replicates | |
| KMS20130509I | 8-HQ and BIT thermal | 2% | | 1.5% | 1.5% | | 3 replicates |
| KMS20130509R | FSi, TMOS, 8-HQ and BIT MW'd | 2% | 4% | 1.5% | 1.5% | 3 replicates | |
| KMS20130509S | FSi, TMOS, 8-HQ and BIT thermal | 2% | 4% | 1.5% | 1.5% | | 3 replicates |

Testing was completed by September 27, 2013. The summary of the results indicates that for the GD samples, the R and S samples had the lowest permeation, and D was almost as good. This result indicates that the repellent materials (FSi treated) are less permeable than the nonrepellent materials, unlike the previous set of samples (KMS130209). There was more permeation for HD than GD.

The Headspace vial-in-vial GC method was used as described. For spiking, a quantity of 10-50 µg of GD or HD (10-50 µl of a 1 mg/ml solution for GD, or 10 µl of a 5 mg/ml solution for HD) was deposited in the small 1-ml vial. The solvent was allowed to evaporate for 15 min. Using the 50-µg dose of agent and 6 mm diameter of fabric, the area is 0.283 $cm^2$, and the dose is 50 µg/0.283 $cm^2$ = 1.8 $g/m^2$.

For the first set of runs (with HD agent), a circle of the test fabric 5/16” in diameter was cut. However, the ePTFE was very thin and flimsy, and it appeared that it might be damaged by the crimping of the vial cap or it might not seal well. So the process was modified for subsequent sample sets to use two ply of the polymer and place it on top of a blank NyCo fabric circle to support it. The polymer was placed on top of and next to the inner vial, with the fabric circle over it and the crimp cap on top.

Each sample set was analyzed multiple times over time from 1 to 5 days to look for time-dependent permeation. All the data for the treated fabrics in the sample sets is compared to the comparable signal for the untreated reference material A.

Fabrics were stored at ambient humidity of about 50% RH. Reactivity of the fabrics may depend on the humidification, but the study of the effects of humidity wasn't done for this set of experiments.

For GD, the pulsed FPD was operated in conditions that were recommended for phosphorus detection, using a phosphorus filter and a data collection window of 4-10 msec after the pulse. The phosphorus calibration is linear, so it is a simple matter to find the ratio of permeation by using the simple ratio of the signal. The injection port was held at 200°C during the injection using a 5:1 split. For HD, the pulsed FPD was operated using conditions for sulfur detection, using a sulfur filter and data collection window of 6-20 msec. The calibration for sulfur has a quadratic calibration curve, or amount varies as the square root of the signal. The pulsed FPD was more sensitive to S than P. In order to obtain unsaturated signal response, it was necessary to use a hot injection port (200°C) and a 100:1 split in the injection port for S detection.

*GD data:* The data for 6 runs of the entire set of samples is shown in Table 18. The column under "area" is the integrated area of the GC peak. The dates and elapsed times after sample prep for the runs are shown. Table 19 consolidates the average processed data for each fabric sample. It includes the average of the signal to the reference signal. The data is plotted in a bar chart in Figure 6.

The final results indicate that the best materials, or the ones with the lowest permeation, are R and S, which are the materials with all treatments including the repellency treatment with FSi. This result is notable because in the last set of treated fabrics, set KMS20130209, the repellent materials had higher permeation than the nonrepellent materials. The R and S materials (7.5 and 12.2% permeation) had lower permeation than D, the next lowest material (22.0%), which only had 8-hydroxyquinoline treatment. The MW (microwaved) samples had lower permeation than the thermal treated samples, supporting the idea that some 8-HQ may evaporate during thermal treatment.

Table 18. Raw data results for Headspace GC permeation tests for GD. Samples for were prepared on 10 Sept. at 10:30 am. Sample KMS20130509A was used as the untreated reference sample, and two replicate reference samples were used for the areas in columns 5 and 6. The last column is the area divided by the average of the two reference samples.

| **fabric** | **time** | **elapsed time (hr)** | **area** | **ref. untr. fabric 1** | **ref. untr. fabric 2** | **rel to untr.** |
|---|---|---|---|---|---|---|
| KMS20130509D | 9/10/2013 19:00 | 8.50 | 0 | 56.9 | 11.85 | 0.0% |
| | 9/10/2013 19:20 | 8.83 | 0 | 56.9 | 11.85 | 0.0% |
| | 9/11/2013 11:40 | 25.17 | 22.9 | 172.3 | 239 | 11.1% |
| | 9/11/2013 17:20 | 30.83 | 19.69 | 156.1 | 172 | 12.0% |
| | 9/12/2013 12:40 | 50.17 | 54.3 | 120.6 | 104.6 | 48.2% |
| | 9/16/2013 11:00 | 144.50 | 15.2 | 25.7 | 24.4 | 60.7% |
| | Average | | 18.68 | | | 22.0% |
| | Std. dev. | | 19.99 | | | |
| KMS20130509E | 9/10/2013 19:40 | 9.17 | 7.45 | 56.9 | 11.85 | 21.7% |
| | 9/10/2013 20:00 | 9.50 | 5.68 | 56.9 | 11.85 | 16.5% |
| | 9/11/2013 12:00 | 25.50 | 78.4 | 172.3 | 239 | 38.1% |
| | 9/11/2013 17:40 | 31.17 | 86 | 156.1 | 172 | 52.4% |
| | 9/12/2013 13:00 | 50.50 | 154.4 | 120.6 | 104.6 | 137.1% |
| | 9/16/2013 11:20 | 144.83 | 31.8 | 25.7 | 24.4 | 126.9% |
| | Average | | 60.62 | | | 65.5% |
| | Std. dev. | | 57.33 | | | |
| KMS20130509F | 9/10/2013 20:20 | 9.83 | 19.51 | 56.9 | 11.85 | 56.8% |
| | 9/10/2013 20:40 | 10.17 | 16.19 | 56.9 | 11.85 | 47.1% |
| | 9/11/2013 12:20 | 25.83 | 103.3 | 172.3 | 239 | 50.2% |
| | 9/11/2013 18:00 | 31.50 | 49 | 156.1 | 172 | 29.9% |
| | 9/12/2013 13:20 | 50.83 | 149.1 | 120.6 | 104.6 | 132.4% |
| | 9/16/2013 11:40 | 145.17 | 70.2 | 25.7 | 24.4 | 280.2% |
| | Average | | 67.88 | | | 99.4% |
| | Std. dev. | | 51.43 | | | |
| KMS20130509G | 9/10/2013 21:00 | 10.50 | 79.2 | 56.9 | 11.85 | 230.4% |
| | 9/10/2013 21:20 | 10.83 | 80 | 56.9 | 11.85 | 232.7% |
| | 9/11/2013 12:40 | 26.17 | 223 | 172.3 | 239 | 108.4% |
| | 9/11/2013 18:20 | 31.83 | 83.8 | 156.1 | 172 | 51.1% |
| | 9/12/2013 13:40 | 51.17 | 158.6 | 120.6 | 104.6 | 140.9% |
| | 9/16/2013 12:00 | 145.50 | 54.1 | 25.7 | 24.4 | 216.0% |
| | Average | | 113.12 | | | 163.2% |
| | Std. dev. | | 64.39 | | | |
| KMS20130509H | 9/10/2013 21:40 | 11.17 | 3.82 | 56.9 | 11.85 | 11.1% |
| | 9/10/2013 22:00 | 11.50 | 2.87 | 56.9 | 11.85 | 8.3% |
| | 9/11/2013 13:00 | 26.50 | 22.9 | 172.3 | 239 | 11.1% |
| | 9/11/2013 18:40 | 32.17 | 49.6 | 156.1 | 172 | 30.2% |
| | 9/12/2013 14:00 | 51.50 | 81.6 | 120.6 | 104.6 | 72.5% |
| | 9/16/2013 12:20 | 145.83 | 15.38 | 25.7 | 24.4 | 61.4% |
| | Average | | 29.36 | | | 32.4% |

| | | | | | | |
|---|---|---|---|---|---|---|
| | Std. dev. | | 30.76 | | | |
| KMS20130509I | 9/10/2013 22:20 | 11.83 | 3.76 | 56.9 | 11.85 | 10.9% |
| | 9/10/2013 22:40 | 12.17 | 3.78 | 56.9 | 11.85 | 11.0% |
| | 9/11/2013 13:20 | 26.83 | 22.9 | 172.3 | 239 | 11.1% |
| | 9/11/2013 19:00 | 32.50 | 26.3 | 156.1 | 172 | 16.0% |
| | 9/12/2013 14:20 | 51.83 | 108.5 | 120.6 | 104.6 | 96.4% |
| | 9/16/2013 12:40 | 146.17 | 18.76 | 25.7 | 24.4 | 74.9% |
| | Average | | 30.67 | | | 36.7% |
| | Std. dev. | | 39.31 | | | |
| KMS20130509R | 9/10/2013 23:00 | 12.50 | 2.73 | 56.9 | 11.85 | 7.9% |
| | 9/10/2013 23:20 | 12.83 | 0 | 56.9 | 11.85 | 0.0% |
| | 9/11/2013 13:40 | 27.17 | 22.9 | 172.3 | 239 | 11.1% |
| | 9/11/2013 19:20 | 32.83 | 5.14 | 156.1 | 172 | 3.1% |
| | 9/12/2013 14:40 | 52.17 | 17.2 | 120.6 | 104.6 | 15.3% |
| | 9/16/2013 13:00 | 146.50 | 8.03 | 25.7 | 24.4 | 32.1% |
| | Average | | 9.33 | | | 7.5% |
| | Std. dev. | | 8.90 | | | |
| KMS20130509S | 9/10/2013 23:40 | 13.17 | 3.9 | 56.9 | 11.85 | 11.3% |
| | 9/11/2013 0:00 | 13.50 | 5.8 | 56.9 | 11.85 | 16.9% |
| | 9/11/2013 14:00 | 27.50 | 22.9 | 172.3 | 239 | 11.1% |
| | 9/11/2013 19:40 | 33.17 | 15.5 | 156.1 | 172 | 9.4% |
| | 9/12/2013 15:00 | 52.50 | 13.6 | 120.6 | 104.6 | 12.1% |
| | 9/16/2013 13:20 | 146.83 | 13.3 | 25.7 | 24.4 | 53.1% |
| | Average | | 12.50 | | | 12.2% |
| | Std. dev. | | 6.9 | | | |

Table 19. Summary of results for the samples shown in Table 17. Processed data for the ratio of permeation of treated to untreated control fabric for Headspace GC permeation tests for GD.

| **fabric** | **Ratio of treated to untreated materials** |
|---|---|
| KMS20130509D | 22.0% |
| KMS20130509E | 65.5% |
| KMS20130509F | 99.4% |
| KMS20130509G | 163.2% |
| KMS20130509H | 32.4% |
| KMS20130509I | 36.7% |
| KMS20130509R | 7.5% |
| KMS20130509S | 12.2% |

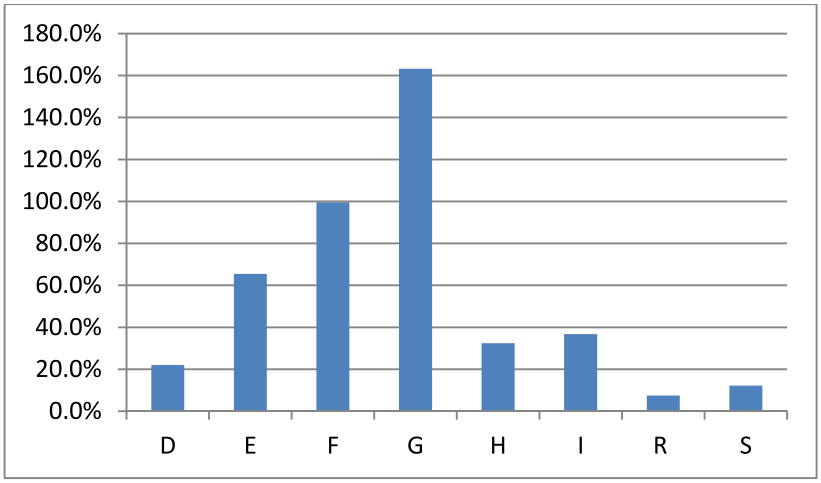



Figure 6. Bar chart of the average permeation data for the ePTFE treated materials with GD relative to untreated material from the data in Table 19.

Some of the data in Table 18 indicates that there may have been saturation of the material or breakthrough of the agent, because the signal for the treated materials increases at later times compared to the reference material. In particular, sample D has no signal for the first two runs, but the signal increases in later runs.

To test to see whether the materials have breakthrough, a smaller set of samples was run at faster sampling rate. The agent challenge was decreased from 50 µg to 10 µg in case the amount of agent was overloading the capacity of the material. The decrease in challenge was also done to decrease the amount of solvent in the inner vial, since incomplete evaporation of the solvent could cause suppressed vapor pressure of the agent to cause an apparent decrease in the vapor pressure. The data is plotted in Figure 7 for the reference sample A and samples D, I, and R. Sample S was also run but wasn't plotted, because the signal for S was below the integration limits (2 units, or less than 1%) for the entire run. The results indicate that there is no observable breakthrough of the agent, since all the traces decrease monotonically and the agent doesn't show increase in absolute signal. The signal for the treated fabrics decreases slower than the decrease for the reference material. This trend is clear for sample I, for which the ratio increases from 14% at 2 hr to 60% at 60 hr. So there is a trend to increase for the treated fabrics, but there is not a dramatic increase characteristic of agent breakthrough.

The general trend of decreasing agent signal over time is attributed to the escape of agent from the outer vial or the decontamination of the agent from reaction with water on the glass in the outer vial. The relative increase of signal for the treated fabrics may indicate that the material is less permeable to physical transport so it escapes from the inner vial slower than for the untreated fabric. However, more detailed studies are needed to confirm this attribution.

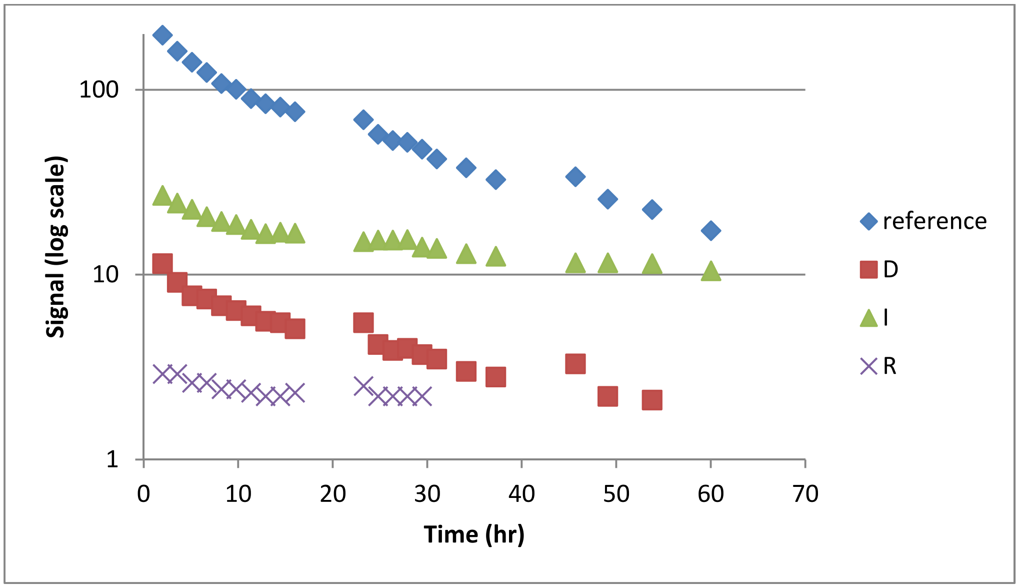



Figure 7. Decrease in signal for GD for the reference material relative to the treated materials 20130509D, I, and R, using an agent challenge of 10 μg (0.18 g/m$^2$). The signal is plotted on a log scale. The trace indicates that breakthrough of the agent isn't occurring.

*HD Data*: The data for several runs of two sets of samples is shown in Table 20. Each set of samples of each fabric type was rerun repeatedly over 4 days. The sample set #1 had two plies of material with a backing layer of untreated cloth for support. Unfortunately, there were fewer repeated runs for this sample set because of instrument problems. The sample set #2, which was actually the first set that was prepared, had only one ply of material and no backing cloth for support. Because the material was not physically strong, it seemed possible that there were physical openings in the material that could allow the agent to diffuse through. The ratio of the signal for the treated fabric to the average of two untreated fabrics is shown in the right column.

Table 21 shows the summary of the average results. None of the materials show results that are as good as they were for GD. The lowest permeation was for sample S, for which the average signal was 28.2% relative to the untreated material, which is promising. However, some care has to be taken to interpret the data. High signals (>400) could have some distortion from signal saturation, so the reference signals may be higher than the measurement indicates, making the ratio too high. But the data is not corrected for the square root signal dependence, which would make the ratio lower.

In general, the HD agent challenge may be too high. Like the GD results, a lower challenge of HD may be closer to the capacity of the fabric and could show stronger effects.

Table 20. Raw data results for Headspace GC permeation tests for HD. Sample set 1 was prepared on 4 Sept. at 10:00 am, and sample set 2 was prepared on 28 August at 11:20 am. Sample KMS20130509A was used as the untreated reference sample, and two replicate reference samples were used for the areas in columns 5 and 6. The last column is the area divided by the average of the two reference sample.

| fabric | time | time after start (hr) | area | ref. untr. fabric 1 | ref. untr. fabric 2 | rel to untr. |
|---|---|---|---|---|---|---|
| KMS20130509D | 9/4/2013 16:00 | 6.00 | 227 | 479 | 469 | 47.9% |
| | 9/5/2013 12:20 | 26.33 | 32.8 | 68.9 | 73.8 | 45.9% |
| | 9/5/2013 17:40 | 31.67 | 23.7 | 50.1 | 52.2 | 46.3% |
| | 9/6/2013 16:40 | 54.67 | 8.18 | 19.6 | 20.8 | 40.5% |
| | 8/29/2013 11:20 | 24.00 | 375 | 584 | 552 | 66.0% |
| | 8/29/2013 18:40 | 31.33 | 476 | 585 | 573 | 82.2% |
| | 8/30/2013 12:00 | 48.67 | 532 | 644 | 657 | 81.8% |
| | 9/3/2013 13:20 | 146.00 | 52.3 | 26.1 | 415 | 23.7% |
| | | | | | | 54.3% |
| KMS20130509E | 9/4/2013 16:20 | 6.33 | 427 | 479 | 469 | 90.1% |
| | 9/5/2013 12:40 | 26.67 | 51.4 | 68.9 | 73.8 | 72.0% |
| | 9/5/2013 17:40 | 31.67 | 43.6 | 50.1 | 52.2 | 85.2% |
| | 9/6/2013 17:00 | 55.00 | 13.9 | 19.6 | 20.8 | 68.8% |
| | 8/29/2013 11:40 | 24.33 | 188 | 584 | 552 | 33.1% |
| | 8/29/2013 19:00 | 31.67 | 236 | 585 | 573 | 40.7% |
| | 8/30/2013 12:20 | 49.00 | 15.8 | 644 | 657 | 2.4% |
| | 9/3/2013 13:40 | 146.33 | 0 | 26.1 | 415 | 0.0% |
| | | | | | | 65.0% |
| KMS20130509F | 9/4/2013 16:40 | 6.67 | 504 | 479 | 469 | 106.3% |
| | 9/5/2013 13:00 | 27.00 | 59.2 | 68.9 | 73.8 | 82.9% |
| | 9/6/2013 17:20 | 55.33 | 15.7 | 19.6 | 20.8 | 77.7% |
| | 8/29/2013 12:00 | 24.67 | 517 | 584 | 552 | 91.0% |
| | 8/29/2013 19:20 | 32.00 | 613 | 585 | 573 | 105.9% |
| | 8/30/2013 12:40 | 49.33 | 633 | 644 | 657 | 97.3% |
| | 9/3/2013 14:00 | 146.67 | 354 | 26.1 | 415 | 160.5% |
| | | | | | | 93.5% |
| KMS20130509G | 9/4/2013 17:00 | 7.00 | 445 | 479 | 469 | 93.9% |
| | 9/6/2013 17:40 | 55.67 | 15.1 | 19.6 | 20.8 | 74.7% |
| | 8/29/2013 12:20 | 25.00 | 491 | 584 | 552 | 86.4% |
| | 8/29/2013 19:40 | 32.33 | 592 | 585 | 573 | 102.2% |
| | 8/30/2013 13:00 | 49.67 | 628 | 644 | 657 | 96.5% |
| | 9/3/2013 14:20 | 147.00 | 133 | 26.1 | 415 | 60.3% |
| | | | | | | 85.7% |

| | | | | | | |
|---|---|---|---|---|---|---|
| KMS20130509H | 9/4/2013 17:20 | 7.33 | 133 | 479 | 469 | 28.1% |
| | 9/6/2013 18:00 | 56.00 | 15.5 | 19.6 | 20.8 | 76.7% |
| | 8/29/2013 12:40 | 25.33 | 342 | 584 | 552 | 60.2% |
| | 8/29/2013 20:00 | 32.67 | 499 | 585 | 573 | 86.2% |
| | 8/30/2013 13:20 | 50.00 | 595 | 644 | 657 | 91.5% |
| | 9/3/2013 14:40 | 147.33 | 82.5 | 26.1 | 415 | 37.4% |
| | | | | | | 63.3% |
| KMS20130509I | 9/4/2013 17:40 | 7.67 | 165 | 479 | 469 | 34.8% |
| | 9/6/2013 18:20 | 56.33 | 11.3 | 19.6 | 20.8 | 55.9% |
| | 8/29/2013 13:00 | 25.67 | 329 | 584 | 552 | 57.9% |
| | 8/29/2013 20:20 | 33.00 | 499 | 585 | 573 | 86.2% |
| | 8/30/2013 13:40 | 50.33 | 580 | 644 | 657 | 89.2% |
| | 9/3/2013 15:00 | 147.67 | 72.3 | 26.1 | 415 | 32.8% |
| | | | | | | 59.5% |
| KMS20130509R | 9/4/2013 18:00 | 8.00 | 185 | 479 | 469 | 39.0% |
| | 9/6/2013 18:40 | 56.67 | 22.4 | 19.6 | 20.8 | 110.9% |
| | 8/29/2013 13:20 | 26.00 | 290 | 584 | 552 | 51.1% |
| | 8/29/2013 20:40 | 33.33 | 439 | 585 | 573 | 75.8% |
| | 8/30/2013 14:00 | 50.67 | 516 | 644 | 657 | 79.3% |
| | 9/3/2013 15:20 | 148.00 | 57.4 | 26.1 | 415 | 26.0% |
| | | | | | | 71.2% |
| KMS20130509S | 9/4/2013 18:20 | 8.33 | 191 | 479 | 469 | 40.3% |
| | 9/6/2013 16:40 | 54.67 | 14.4 | 19.6 | 20.8 | 71.3% |
| | 8/29/2013 13:40 | 26.33 | 102 | 584 | 552 | 17.9% |
| | 8/29/2013 21:00 | 33.67 | 66 | 585 | 573 | 11.4% |
| | 8/30/2013 14:20 | 51.00 | 0 | 644 | 657 | 0.0% |
| | 9/3/2013 15:40 | 148.33 | 1.11 | 26.1 | 415 | 0.5% |
| | | | | | | 28.2% |

Table 21. Summary of results for the samples shown in Table 17. Processed data for the ratio of permeation of treated to untreated control fabric for Headspace GC permeation tests for HD.

| **fabric** | **Ratio of treated to untreated materials** |
|---|---|
| KMS20130509D | 54.3% |
| KMS20130509E | 65.0% |
| KMS20130509F | 93.5% |
| KMS20130509G | 85.7% |
| KMS20130509H | 63.3% |
| KMS20130509I | 59.5% |
| KMS20130509R | 71.2% |
| KMS20130509S | 28.2% |

In conclusion, permeation of GD shows a significant difference between the treated fabrics and the untreated fabric reference, particularly for the lower challenge amount of 10 µg. The best materials were samples R and S, and D was almost as good. This indicates that repellent materials treated with FSi can perform as well or better than nonrepellent materials, which is different from a previous set of samples KMS20130209.

HD shows less difference between untreated materials, although the repellent fabric S has the lowest permeation of the set.

REFERENCES

[1] G. Winfield, "Suitably Dressed," *CBRNe World*, Autumn 2010, 72-76. http://www.cbrneworld.com/_uploads/download_magazines/CBRNe_world_autumn_2010_Suitably_dressed.pdf

[2] D. McGarvey and W. Creasy, *Headspace Gas Chromatography (GC) Method for Studies of Reaction and Permeation of Volatile Agents with Solid Materials*, Edgewood Chemical Biological Center Technical Report ECBC-TR-1280, Aberdeen Proving Ground-Edgewood Area, MD, Jan. 2015. Approved for public release.

[3] B. Ashley, W. B. Salter, K. M. Simpson, G. Strack, N. Pomerantz, W. Creasy, G. Strouse, and J. R. Owens, "Mechanistic Study of Novel Schiff Base CWA Decomposition Catalysts," poster presented at the 2015 Chemical and Biological Defense Science and Technology Conference, St. Louis, MO, May 11-14, 2015.

[4] A. Judd, B. Blackstone, and B. McVeety, *Chemical/Biological Agent Resistance Test (CBART) Test Fixture System Verification and Analytical Monitoring System Development (CBART Phase III) Final Report*, Battelle Memorial Institute Report Number 55893-CH.1, Battelle Memorial Institute, Columbus, OH, March 16, 2011. Approved for public release. http://www.dtic.mil/dtic/tr/fulltext/u2/a546890.pdf

[5] P. G. Hill and R. M. Smith, "Determination of sulphur compounds in beer using headspace solid-phase microextraction and gas chromatographic analysis with pulsed flame photometric detection," J. Chromatogr. A, 872 (2000) 203-213.

[6] P. A. Vazquez-Landaverde, J. A. Torres, and M. C. Qian, “Quantification of Trace Volatile Sulfur Compounds in Milk by Solid-Phase Microextraction and Gas Chromatography-Pulsed Flame Photometric Detection,” J. Dairy Sci. 89 (2006) 2919-2927.

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